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# Flue Gas Desulfurization Pilot Study. Phase I Survey of Major Installations. Appendix 95-C Double Alkali/Sludge Flue Gas Desulfurization Process

NATO Committee on the Challenges of Modern Society, Brussels (Belgium)

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COMMITTEE ON THE CHALLENGES
OF MODERN SOCIETY

# Flue Gas Desulfurization Pilot Study Phase I — Survey of Major Installations - Double Alkali/Sludge Flue Gas Desulfurization Process

## Appendix 95-C

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PHASE I

# Flue Gas Desulfurization Pilot Study Phase I

# Survey of Major Installations - Double Alkali/ Sludge Flue Gas Desulfurization Process

APPENDIX 95-C

Lead Country - United States

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## SUMMARY

The double alkali system is a relatively new flue gas desulfurization (FGD) process that was developed to overcome some of the problems associated with lime/limestone systems without losing any of their advantages. The problems generally associated with lime/limestone systems are scaling, plugging, and erosion, all of which result from the absorbant's being in slurry form. The double alkali system overcomes these problems by using a soluble absorbant. The inexpensive raw materials and the relatively simple processing steps that are the major advantages of the lime/limestone systems are also advantages of the double alkali system. Pilot plant investigations on the application of double alkali to combustion sources began in 1973. Now three utilities, with a total capacity of 1102 MW, and three industrial-sized boilers in the United States are installing this system.

The double alkali/sludge system is applicable to areas with adequate land for sludge disposal and locally available inexpensive lime or limestone. The system is well developed, does not require high particulate control, is very flexible

in adapting to different $SO_2$ concentrations, and is in the lower cost range. Although operational experience is limited, available information indicates a good maintenance and availability record.

In the double alkali/sludge system, $SO_2$ is absorbed by a solution of sodium sulfite and water, thereby forming sodium bisulfite. This solution is pumped to separate reaction tanks where lime or limestone is added. The sodium bisulfite decomposes to sodium sulfite and $SO_2$; the $SO_2$ reacts with the calcium and forms calcium sulfite. The sodium sulfite is returned to the scrubber, and the calcium sulfite is precipitated and disposed of. A small amount of sodium is lost with the calcium sulfite sludge and must be replenished with fresh NaOH or $Na_2CO_3$. A small amount of calcium ion dissolves in the sodium sulfite solution and must be removed to prevent scaling in the scrubber.

Because the process is based on a dissolved absorbant (generally NaOH), scaling and plugging are not a problem; therefore, scrubbers in double alkali systems do not require the elaborate contacting surfaces of lime and limestone systems. However, chloride ion is normally present, especially in coal-fired boiler systems; and corrosion can be a problem if proper materials are not selected.

The recent rapid development of lime and limestone systems will tend to restrict the use of double alkali to

plants requiring 98 percent $SO_2$ removal or low maintenance and high availability. These would include small-peak-load utility boilers and industrial boilers, or other operations located in or near highly populated areas.

The advantages and disadvantages of this system are summarized below:

Advantages

1. The soluble product in the absorber minimizes solids buildup and erosion problems, thereby probably offering high system availability.
2. The system is capable of very high $SO_2$ removal efficiencies.
3. Because particulates are removed in the quenching and scrubbing stage, the process permits removal of $SO_2$ and particulates.
4. Because absorption takes place in the scrubber in an unsaturated solution, the absorbant has a large absorption capacity.
5. The scrubber requires a relatively low liquid-to-gas (L/G) ratio.
6. Corrosion and erosion problems are minor compared with those in wet lime/limestone processes.
7. The system can tolerate a high fly ash content.

Disadvantages/Problems

1. Large quantities of sludge containing calcium sulfite and sulfate must be disposed of in an acceptable manner.
2. Design complexities must be introduced to deal with the following problems:
   (a) The necessity to avoid excessive purge of alkali sulfate produced as a result of oxidation of the sulfite. (Alkali sulfate is difficult to regenerate.)

(b) The necessity to avoid scrubbing with the clear liquor saturated with calcium sulfate (excessively high levels of calcium sulfate could lead to scaling problems).

3. Some makeup is necessary to replenish sodium losses.

4. Most work to date has been on lime-double alkali systems; lime is more expensive and requires significant quantities of energy for its production from limestone.

# 1.0 BACKGROUND AND INTRODUCTION

This report is one of a series on the status of flue gas desulfurization processes in the NATO countries and Japan. In this program, the United States, the Federal Republic of Germany, and Norway have acted as lead countries in gathering information and the preparation of the reports.

The double alkali process is an indirect lime/limestone system using a soluble regenerable sodium, potassium, ammonium, or aluminum salt solution as the absorbant. The $SO_2$ is absorbed by the solution and then reacted with a lime/limestone slurry in a separate reactor. This process was developed primarily to overcome the scaling and plugging problems associated with direct lime/limestone processes.

Envirotech installed one of the first pilot plant units using this system on a combustion source at the Gadsby Station of Utah Power. The unit size was only 1 MW. In 1974, after extensive pilot plant testing, General Motors Corporation at Parma, Ohio, began using a double alkali FGD system on a 32-MW, coal-fired boiler. In the same year, Caterpillar Tractor Company began using one on an 18-MW,

coal-fired boiler at their Joliet, Illinois, plant. The Southern Company, through its subsidiary Gulf Power Company, started a demonstration plant at the Scholz Power Station at Sneads, Florida, in 1975. The FGD was installed on a 20-MW unit, and it operated successfully through mid-1976. In 1975, Caterpillar installed three more units to control $SO_2$ emissions from a total of 57-MW at its Mossville, Illinois, plant; they plan to install double alkali systems at three other manufacturing plants. Installation of this type of system at three separate utility companies is in various stages of completion. The power stations involved are Central Illinois, Newton No. 1; Louisville G&E, Cane Run No. 6; and Southern Indiana G&E, A.B. Brown No. 1. All the units (except Utah Power) burn coal with a minimum of 2.5 percent sulfur content. Japan has many double alkali systems operating, but all of them produce gypsum.

Five industrial boilers and one metallurgical kiln are operating double alkali/sludge FGD systems for $SO_2$ emission control.

## 2.0 GENERAL PROCESS DESCRIPTION

A double alkali system is an indirect lime/limestone scrubbing system that cleans flue gas by a method that avoids the plugging and scaling problems generally associated with direct lime/limestone scrubbing systems. The indirect technique involves absorbing $SO_2$ by a soluble alkaline medium in the scrubbing chamber and treating the scrubber effluent with lime or limestone in a separate reactor outside the scrubber loop. Calcium sulfites and sulfates are precipitated and discarded, whereas the scrubbing liquor is regenerated and returned to the scrubbing loop. Figure 1 shows an example 500-MW, coal-fired boiler with a double alkali/sludge FGD system.

### 2.1 PROCESS CHEMISTRY

#### 2.1.1 Absorption

Removal of $SO_2$ is effected in the gas scrubber by the reaction of the gas with a circulating alkaline solution sprayed countercurrently to the gas flow. Although the scrubbing liquor is generally a sodium solution made up of sodium hydroxide (NaOH) and sodium sulfite ($Na_2SO_3$), it can be an alkali of potassium, ammonium, or aluminum.

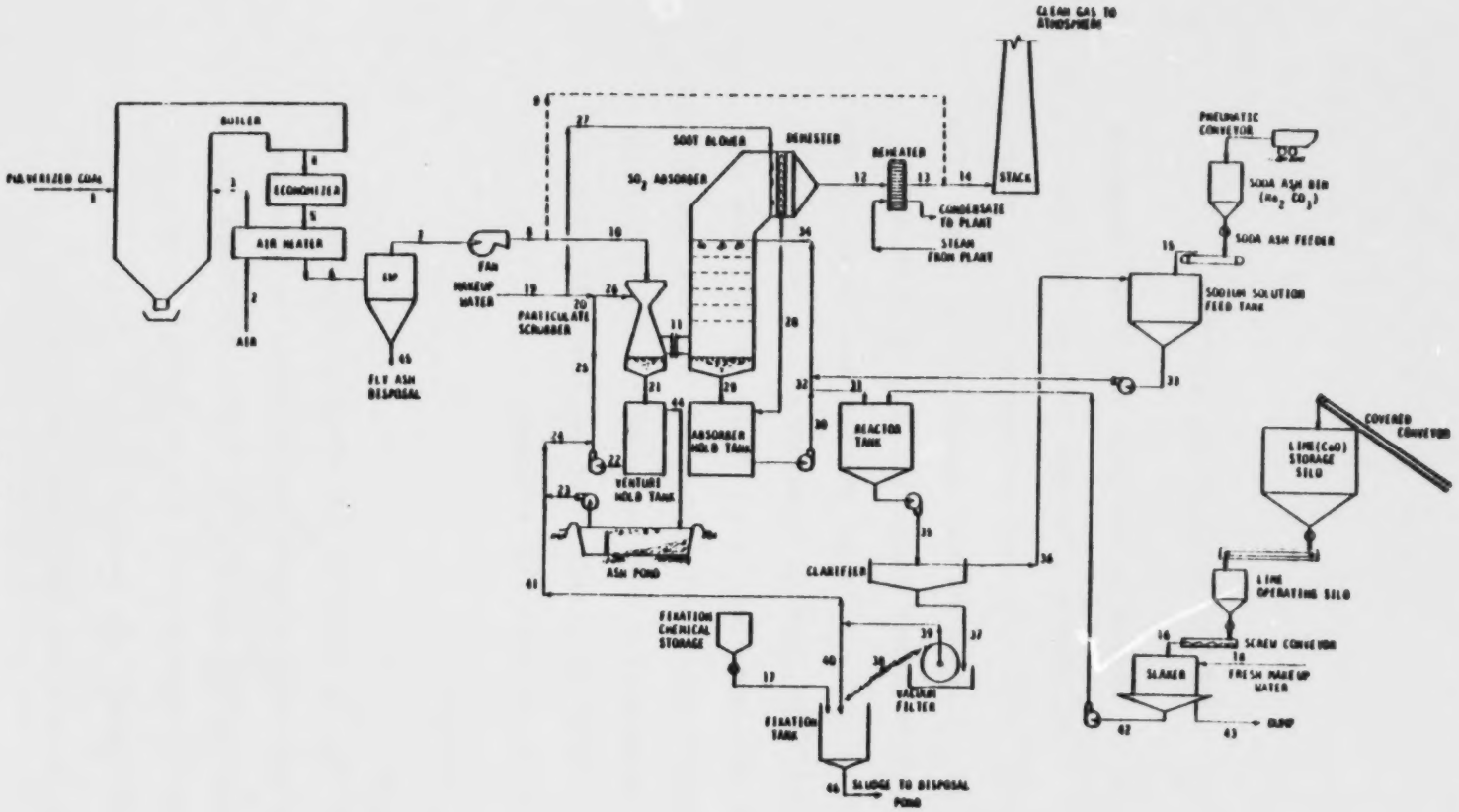


Figure 1. Process flow diagram and material balance for 500-MW, coal-fired boiler and a double alkali/sludge desulfurization process. (See notes at end of figure.) (continued)

| Stream no. | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Description | Coal to boiler | Air to air heater | Air to boiler | Gas to economizer | Gas to air heater | Gas to ESP | Gas to fan | Fan outlet gas | Gas bypass | Gas to part. scrbr. | Gas to $SO_2$ absorber | Gas to reheater |
| Rate, 1000 kg/h | 170 | 2049 | 1848 | 1998 | 1998 | 2199 | 2186 | 2186 | 77.3 | 2109 | 2196.6 | 2180.8 |
| $Nm^3/s$ | | 464 | 419 | 445 | 445 | 490 | 490 | 490 | 17 | 473 | 503 | 501.4 |
| $m^3/s$, Liquid | | | | | | | | | | | | |
| Particulates, kg/h | | | | 15,300 | 15,300 | 15,300 | 2600 | 2600 | 91 | 2510 | 12.2 | 12.2 |
| Temperature, °C | | 43.3 | 279 | 477 | 374 | 154 | | | | | 51.7 | 51.7 |
| Specific gravity | | | | | | | | | | | | |
| Viscosity, pascal-second | | | | | | | | | | | | |
| Undissolved solids, % | | | | | | | | | | | | |
| pH | | | | | | | | | | | | |
| Sulfur as $SO_2$, kg/h | 11,900 | | | 11,900 | 11,900 | 11,900 | 11,900 | 11,900 | 420 | 11,480 | 10,330 | 770 |

| Stream no. | 13 | 14 | 15 | 16 | 17 | 18 | 19 | 20 | 21 | 22 |
|---|---|---|---|---|---|---|---|---|---|---|
| Description | Reheater discharge gas | Gas to stack | Soda ash to feed tank | Lime to slaker | Chemical to fixation tank | Fresh makeup water | Fresh makeup water | Makeup water to venturi | Part. scrbr. slurry to hold tank | Recycle from hold tank |
| Rate, 1000 kg/h | 2180.8 | 2258.1 | 0.790 | 11.46 | 4.58 | 62 | 50.76 | 44.16 | 4515 | 4465 |
| $Nm^3/s$ | 501.4 | 518.4 | | | | | | | | |
| $m^3/s$, Liquid | | | | | | 0.0172 | 0.041 | 0.0123 | 1.218 | 1.204 |
| Particulates, kg/h | 103.2 | 103.2 | | | | | | | 225,790 | 223,250 |
| Temperature, °C | 78.9 | 78.9 | | | | | | | | |
| Specific gravity | | | | | | 1.0 | 1.0 | 1.0 | 1.03 | 1.03 |
| Viscosity, pascal-second | | | | | | | | | | |
| Undissolved solids, % | | | | | | -0- | -0- | -0- | 5 | 5 |
| pH | | | | | | | | | | |
| Sulfur as $SO_2$, kg/h | 770 | 1190 | | | | | | | 101,700 | 102,520 |

Figure 1 (continued).

| Stream no. | 23 | 24 | 25 | 26 | 27 | 28 | 29 | 30 | 31 | 32 |
|---|---|---|---|---|---|---|---|---|---|---|
| Description | Pond recycle water | | | Scrubber to part. scrbr. | Demister wash water | Demister wash to hold tank | Spent slurry to hold tank | Recycle from hold tank | Purge to reactor tank | |
| Rate, 1000 kg/h | 45.44 | 88.24 | 4553.24 | 4597.6 | 6.6 | 6.6 | 4900.2 | 4906.8 | 110.2 | 4796.6 |
| $Mg^3/s$ | | | | | | | | | | |
| $m^3/s$, Liquid | 0.0126 | 0.0245 | 1.228 | 1.240 | 0.00183 | 0.00183 | 1.361 | 1.363 | 0.0306 | 1.332 |
| Particulates, kg/h | | | 223,250 | 223,250 | | | | | | |
| Temperature, °C | | | | | | | | | | |
| Specific gravity | 1.0 | 1.0 | 1.03 | 1.03 | 1.0 | 1.0 | | 1.0 | 1.0 | 1.0 |
| Viscosity, pascal-second | | | | | | | | | | |
| Undissolved solids, % | -0- | -0- | 5 | 5 | | -0- | | | | |
| pH | | | | | | | | | | |
| Sulfur as $SO_2$, kg/h | | | 102,520 | 102,520 | | | | | | |

| Stream no. | 33 | 34 | 35 | 36 | 37 | 38 | 39 | 40 | 41 | 42 |
|---|---|---|---|---|---|---|---|---|---|---|
| Description | Soda solution | Scrubbing slurry to absorber | Clarifier feed | Clarifier overflow | Clarifier underflow | Filter cake | Filtrate | Mixing water | | Slurry to reactor |
| Rate, 1000 kg/h | 92.4 | 4889 | 183.3 | 91.6 | 91.7 | 45.8 | 45.9 | 3120 | 42.8 | 73.13 |
| $Mg^3/.$ | | | | | | | | | | |
| $m^3/s$, Liquid | 0.0257 | 1.3581 | 0.0467 | 0.0254 | 0.0212 | 0.00848 | 0.01275 | 0.00087 | 0.0119 | 0.0185 |
| Particulates, kg/h | | | | | | | | | | |
| Temperature, °C | | | | | | | | | | |
| Specific gravity | 1.0 | 1.0 | 1.09 | 1.0 | 1.20 | 1.5 | 1.0 | 1.0 | 1.0 | 1.1 |
| Viscosity, pascal-second | | | | | | | | | | |
| Undissolved solids, % | -0- | | 15 | -0- | 30 | 60 | -0- | -0- | -0- | 20 |
| pH | 12.3 | | | | | | | | | 12.1 |
| Sulfur as $SO_2$, kg/h | | | | | | | | | | |

Figure 1 (continued).

| Stream no. / Description | 43 Slaker dump | 44 Particulate slurry product | 45 Fly ash disposal | 46 Sludge to disposal pond |
|---|---|---|---|---|
| Rate, 1000 kg/h | 0.340 | 50 | 12.7 | 53.5 |
| $Nm^3/s$ | | | | |
| $m^3/s$, Liquid | | 0.0135 | | 0.0099 |
| Particulates, kg/h | | 2500 | 12,700 | |
| Temperature, °C | | | | |
| Specific gravity | | 0.03 | | |
| Viscosity, pascal-second | | | | 1.5 |
| Undissolved solids, % | | | | 60 |
| pH | | | | |
| Sulfur as $SO_2$, kg/h | | | | |

**Notes:**

Calculations based on:

a. 130% stoichiometric lime: 95% CaO and 5% grit.
b. 60% of the grit is removed.
c. 90% $SO_2$ removal.
d. 90% solid in ash pond.
e. $CaSO_3 \cdot 1/2\ H_2O/CaSO_4 \cdot 2H_2O$ = 40/60 by weight.
f. 15% S in coal (dry).
g. 12% ash coal (as fired).
h. 92% of sulfur in coal evolves as $SO_2$.
i. 75% of ash in coal evolves as fly ash.
j. 99.5% removal of particulates to scrubber.
k. Pond evaporation and seepage equals rainfall.
l. Particulates must be added to flow rate for total mass flow.

Figure 1 (continued).

The scrubber liquor is usually defined, with respect to NaOH concentration, as either concentrated or dilute. Solutions of greater than 0.1 molal of NaOH are considered concentrated. The choice of liquor is based strictly on the oxidation potential of the flue gas. Concentrated systems are more suitable for units with low oxidation rates, such as boilers that burn high-sulfur coal, or large boilers on which excess air is carefully controlled. Dilute systems are better for small boilers, boilers that burn low-sulfur coal, or boilers with large amounts of excess air. The concentrated system, the predominant choice, is described in this report.

Sulfur dioxide is absorbed and produces a spent sodium sulfite/bisulfite liquor according to the following reaction sequence:

$$NaOH + SO_2 \rightarrow NaHSO_3 \quad (1)$$

$$2NaOH + SO_2 \rightarrow Na_2SO_3 + H_2O \quad (2)$$

$$Na_2SO_3 + SO_2 + H_2O \rightarrow 2NaHSO_3 \quad (3)$$

In reaction 1, $SO_2$ is absorbed by the sodium hydroxide to form bisulfite. The same reactants also unite, as shown in reaction 2, to form sodium sulfite, which further absorbs $SO_2$ to form bisulfite in reaction 3. The scrubber liquor is pumped to the lime or limestone regenerator.

### 2.1.2 Regeneration of Scrubbing Solution

The $SO_2$ removed from the flue gas in the form of soluble sodium sulfite-bisulfite is reacted with a lime or limestone slurry, which transfers the $SO_2$ to the lime/limestone slurry, where it reacts to form insoluble calcium sulfite and calcium sulfate. Insoluble calcium sulfite and calcium sulfate are removed by settling and vacuum filtration and then dumped. The regenerated sodium sulfite from the filtrate is "softened" and returned to the scrubber. (Any chemical reaction that removes excess minerals from a solution to reduce the scaling potential is known as "softening.") Additional sodium salts are added to make up for the portion lost in the process.

When limestone (calcium carbonate) is used, regeneration takes place in several stages, as shown in the following series of reactions:

$$NaHSO_3 + CaCO_3 \rightarrow NaHCO_3 + CaSO_3 \quad (4)$$

Because sodium bisulfite is by far the major reactant, the solution remains acidic. In the acid solution, the sodium bicarbonate breaks down to sodium hydroxide and carbon dioxide.

$$NaHCO_3 \rightarrow NaOH + CO_2 \quad (5)$$

The sodium hydroxide then reacts with the excess sodium bisulfite to produce the original scrubbing liquor.

$$NaOH + NaHSO_3 \rightarrow Na_2SO_3 + H_2O \quad (6)$$

The overall regeneration reaction is, therefore,

$$2NaHSO_3 + CaCO_3 \rightarrow Na_2SO_3 + CaSO_3 + H_2O + CO_2 \quad (7)$$

When lime is used for regeneration, it must first be slaked (hydrated).

$$CaO + H_2O \rightarrow Ca(OH)_2 \quad (8)$$

The slaked lime is then pumped to the reactor tank, where the following overall regeneration occurs.

$$2NaHSO_3 + Ca(OH)_2 \rightarrow Na_2SO_3 + CaSO_3 + 2H_2O \quad (9)$$

The lime further reacts with the sodium sulfite and sodium sulfate in solution. These reactions are limited by the equilibrium hydroxide ion concentration and the sulfite ion concentration, which are more active than the sulfate species when forming sodium hydroxide.

$$Na_2SO_3 + Ca(OH)_2 \rightarrow 2NaOH + CaSO_3 \quad (10)$$

$$Na_2SO_4 + Ca(OH)_2 \rightarrow 2NaOH + CaSO_4 \quad (11)$$

2.1.3 Sodium Makeup and Softening

The liquor from the vacuum filter is returned to the scrubbing loop, but not before it has been treated to correct potential problems. Firstly, sufficient sodium or other alkali must be added to the solution to make up for the small percentage of scrubbing liquor lost in the waste stream. Secondly, any excess calcium ion concentration must be reduced to prevent scaling in the scrubber. Both calcium sulfate and calcium sulfite are produced during regeneration (reactions 10 and 11). Since the solubility of calcium

sulfate is approximately two orders of magnitude greater than that of calcium sulfite, calcium sulfate is more likely to remain in solution and be carried in the liquor from the clarifier. In other words, when solid calcium sulfate is present in solution at equilibrium, the regeneration system produces high calcium ion concentrations. Therefore, as conditions develop that cause the scrubbing liquor to become supersaturated with calcium ions, a high potential for scaling occurs in the scrubber.

If limestone regeneration is used, lost sodium is replaced by adding NaOH to the solution. Only enough sodium hydroxide is added to the liquor to compensate for the sodium lost in the waste discharge. Excess calcium can be removed by contacting the solution with a stream of clean boiler flue gas containing carbon dioxide. The carbon dioxide reacts with the calcium ions as presented in the following equation.

$$Ca^{++} + CO_2 + H_2O \rightarrow CaCO_3 + 2H^+ \qquad (12)$$

This reaction reduces the calcium ion concentration to a level below the saturation value, and the liquor can be safely returned to the scrubbing loop. The precipitated calcium carbonate settles out and can be used to regenerate the scrubbing liquor (reaction 7).

The same procedures for replenishing lost sodium and reducing calcium ion concentrations in the liquor may be

used in a lime regeneration system. When using lime, however, an alternate method not applicable to a limestone regeneration system is preferred. In this method, sodium carbonate ($Na_2CO_3$) is added to the liquor from the clarifier; it not only replaces lost sodium, but also softens the solution in a single chemical reaction.

$$Na_2CO_3 + Ca(OH)_2 \rightarrow 2NaOH + CaCO_3 \qquad (13)$$

Sodium is replaced in the scrubbing liquor as sodium hydroxide, and excess calcium is removed as precipitated calcium carbonate. As in the limestone system, only enough sodium is added to the liquor to make up for that lost in the waste discharge. If the amount of sodium carbonate added is insufficient to soften the solution satisfactorily, however, $CO_2$ may be added (as in reaction 12) to complete the softening process.

The makeup soda ash requirement is estimated at 5 percent on a weight basis and can be calculated according to equation 4 and molecular weights:

Makeup soda ash required = $\frac{106}{64} \times \frac{5}{100} = 0.083$ kg/kg of $SO_2$.

Lime is required in the reactor to regenerate sodium solutions. According to equations 8, 9, 10, and 11, theoretical lime requirement = $\frac{56}{64} = 0.875$ kg/kg of $SO_2$. Using 1.1 of stoichiometric requirement and 95 percent lime purity,

the actual lime requirement = $\frac{56}{64} \times \frac{1.1}{0.95}$ = 1.0132 kg/kg of $SO_2$.

The sludge generated at the reactor is similar to that generated in a direct lime or limestone process. The unused lime, lime impurities, and makeup soda ash also combine with the sludge. If equal proportions of calcium sulfate hemihydrate and gypsum are assumed,

$$\text{dry sludge} = \frac{0.5 \times 129 + 0.5 \times 172}{64} + (1.0132-0.875) + 0.083$$

$$= 2.573 \text{ kg/kg of } SO_2$$

2.1.4 Alternative Operating Modes

Flue gas desulfurization systems can use various combinations of the alternative steps described. The five basic modes of operation of sodium/calcium scrubbing are defined below:

1. Limestone and lime regeneration, dilute active alkali, and sulfite softening.
2. Lime regeneration, dilute active alkali, and sulfite softening.
3. Lime regeneration, concentrated active alkali, and side-stream sulfate treatment (removal).
4. Limestone regeneration, concentrated active alkali, and side-stream sulfate treatment (removal).
5. Lime regeneration, dilute active alkali, and carbonate softening.

These modes are discussed briefly in the following sections, and some advantages and disadvantages are noted

for each. Many variations on these five basic schemes can be produced by varying certain parameters associated with the systems.

The first mode is a double-loop (limestone/lime), dilute alkali system. Dilute alkali indicates that the sulfite or alkali concentration entering the scrubber will be less than approximately 0.1 molality. Dilute alkali scrubbing solutions allow sulfate regeneration with lime in this mode of operation. "Double loop" refers to the regeneration method. Spent scrubbing liquor is treated with limestone to neutralize the bisulfite and precipitate calcium sulfite. A stream from this limestone reaction vessel is then treated with lime to precipitate calcium sulfite and sulfate and generate sodium hydroxide.

The relative amount of reaction between lime and the sulfite and sulfate is determined mainly by sulfite and sulfate concentrations and by lime stoichiometry. Liquor from the lime reaction vessel is returned to the limestone reaction vessel to ensure that unsaturated calcium ion concentrations go to the scrubber. The presence of sulfite ion in the limestone reactor causes the desaturation. The reduction of calcium ion concentrations by calcium sulfite precipitation is referred to as "sulfite softening." Sodium carbonate may be added to provide additional softening and make up any sodium losses.

The disadvantages of this scheme are that the reaction with limestone requires relatively long hold times, two major reactors are necessary, and large volumes of relatively dilute scrubbing liquor must be circulated. The advantages are that limestone is relatively inexpensive and can be used for regeneration of both bisulfite and sulfate, and equipment requirements are relatively simple.

The second mode of operation is a double-loop (lime only), dilute alkali system. This arrangement is very similar to that of the first mode. Spent scrubbing liquor is treated with lime to neutralize the bisulfite only. A stream from the lime/bisulfite reaction vessel is then treated with additional lime in a separate vessel to react with sulfite and sulfate, thereby forming calcium solids and sodium hydroxide. Liquor from this second reaction vessel is returned to the lime/bisulfite reaction vessel to ensure unsaturated calcium ion concentrations with respect to calcium sulfate; this is achieved by sulfite softening of the liquors before they enter the scrubber.

The disadvantages of this flow scheme are that it is difficult to control the pH and calcium ion in the regeneration loop (because of the addition of a relatively concentrated strong base i.e. lime, to a dilute solution of a weak acid); the regeneration loop requires two reactors; and

large volumes of relatively dilute scrubbing liquor must be circulated to the scrubber. The advantages are that regeneration with lime requires relatively short hold times, and equipment requirements are relatively simple.

The third mode of operation involves lime regeneration, concentrated alkali solutions, and independent treatment of sulfate removal and control. Lime is used for the bisulfite neutralization of the concentrated (∿0.5 molality) alkali scrubbing solutions. A side stream then is taken from the bisulfite reactor, where sulfuric acid is used to precipitate sulfates and regenerate the scrubbing liquor. Again, sulfite softening is used to remove residual calcium ions. Figure 1 shows a typical flow sheet.

The disadvantage of this third mode is the possibility of sulfate regeneration complications. The advantages are that relatively short hold times are necessary for the bisulfite/sulfite regeneration with lime; utilization of reactants is high; the system is in an advanced state of development; and high $SO_2$ removal efficiencies are achieved with low flows of the concentrated alkali scrubbing liquors. This third mode of operation appears to be very promising, but universal, large-scale, successful application depends on how effective this treatment is for sulfate removal and control.

The fourth mode involves limestone regeneration, concentrated active alkali, and side-stream sulfate removal. This mode differs from the third mode only in that limestone is used instead of lime for the bisulfite-removal step. Like the third mode, it has the possible disadvantage of sulfate regeneration complications, and it has the added disadvantage of limestone's requiring long hold times for the bisulfite/sulfite regeneration. Advantages of this flow scheme are that $SO_2$ removal efficiencies are high, liquor flow rates are low, and utilization of reactants is high. Successful, large-scale application of this flow scheme also depends on how effective the treatment is for sulfate removal and control.

The fifth mode of operation is a lime regeneration, dilute alkali system with carbonate softening for calcium ion (scaling) control. The spent scrubbing liquor is treated with lime to neutralize bisulfite and react with sulfite and sulfate. The only significant difference between this process and the second mode is the use of carbonate softening ($CO_2$ and $Na_2CO_3$) to lower the calcium ion concentration. The disadvantages of this scheme are that it may not regenerate sulfate adequately; it has the potential for scaling; and it must circulate large volumes of relatively dilute scrubbing liquors. The advantages are

that it can deal with high oxidation levels, its equipment requirements are relatively simple, and it is in an advanced state of development.

## 2.2 DESCRIPTION OF EQUIPMENT COMPONENTS

### 2.2.1 Particulate Removal

Before the sulfur oxides are removed, flue gas is passed through a venturi scrubber or an electrostatic precipitator (ESP) and a quenching tower, which removes a large percentage of any particulate matter that may be in the gas stream and cools and humidifies the gas stream. This not only prevents the emission of particulates, but also reduces the potential plugging of trays in the gas scrubbing unit and reduces contamination of the scrubbing liquor and sludge. Particulate scrubbing liquor is kept separate from $SO_2$ scrubbing liquor. The spent particulate scrubbing liquor is pumped to an ash pond, where the fly ash settles and the water is neutralized with lime or limestone, then returned to the venturi. Any dry fly ash from an ESP can be combined with the venturi liquor before disposal.

### 2.2.2 $SO_2$ Absorber

The absorber is the primary $SO_2$ removal unit in the double alkali/sludge FGD system. Each of the many designs has a different method of contacting the flue gas with the slurry. Absorbers for sodium solution scrubbing do not require the exotic design features of lime and limestone

systems, since scaling and plugging are not a problem. The more common unit designs are spray towers (Figure 2), packed towers (Figure 3), venturi scrubbers (Figure 4), and sieve or perforated trays (Figure 5).

As with calcium-based systems, corrosion and pitting can be a problem. Selection of proper materials for the scrubber body and internals is necessary for long life and maintenance-free operation. Materials that have been used for the scrubber body include steel lined with rubber, fiberglass-reinforced polyester (FRP), acid brick or flaked glass, and 316L stainless steel. Materials used for absorber internals include FRP, 316 stainless steel, polyethelene, and polypropylene.

The number and size of scrubber modules per system are directly related to boiler load turndown potential, system availability, and L/G distribution. Boiler loads fluctuate, and the scrubber system must adapt to low loads without reduced performance. Multiple scrubber modules allow the shutdown of individual modules as the boiler load decreases: the more modules there are in the system, the smoother the transition. Because scrubber modules shut down during low boiler loads can be scheduled for maintenance, overall system availability is increased. The smaller cross-sections of smaller modules also make it possible to achieve more

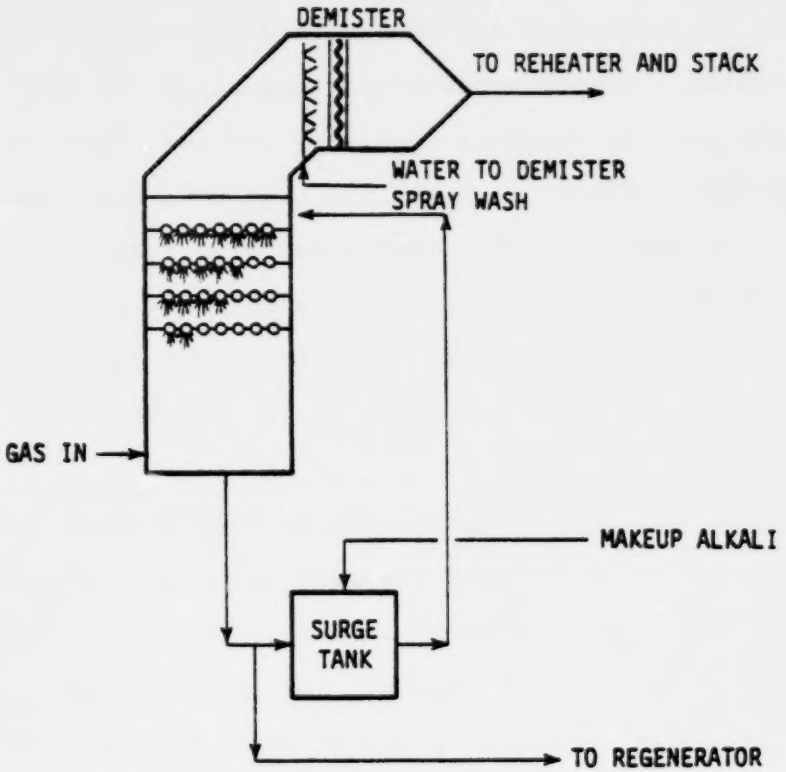


Figure 2. Spray tower.

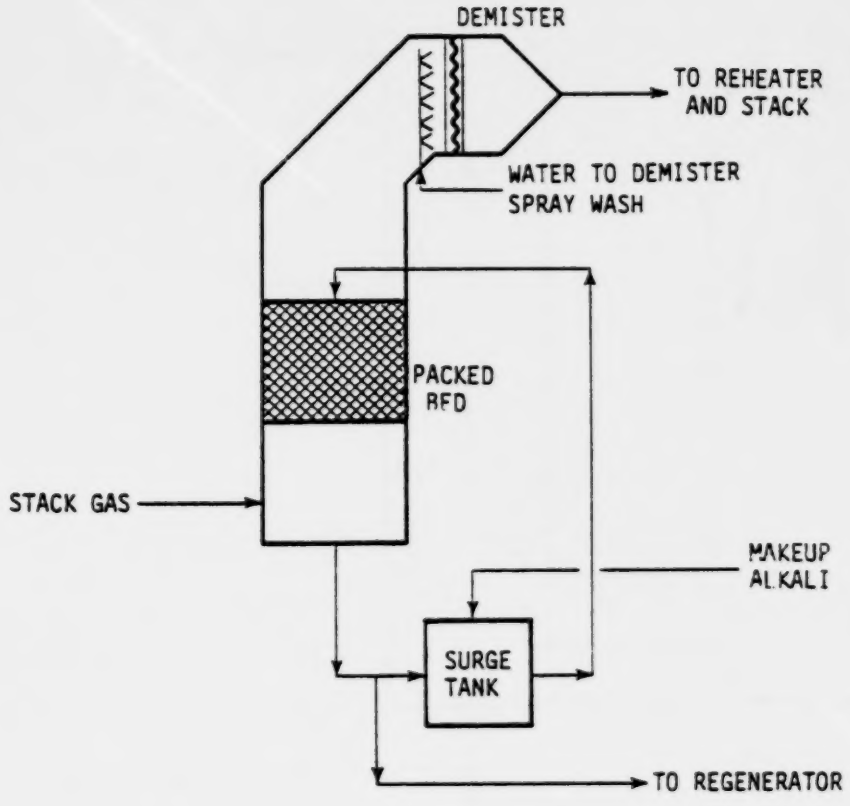


Figure 3. Fixed packing absorber.

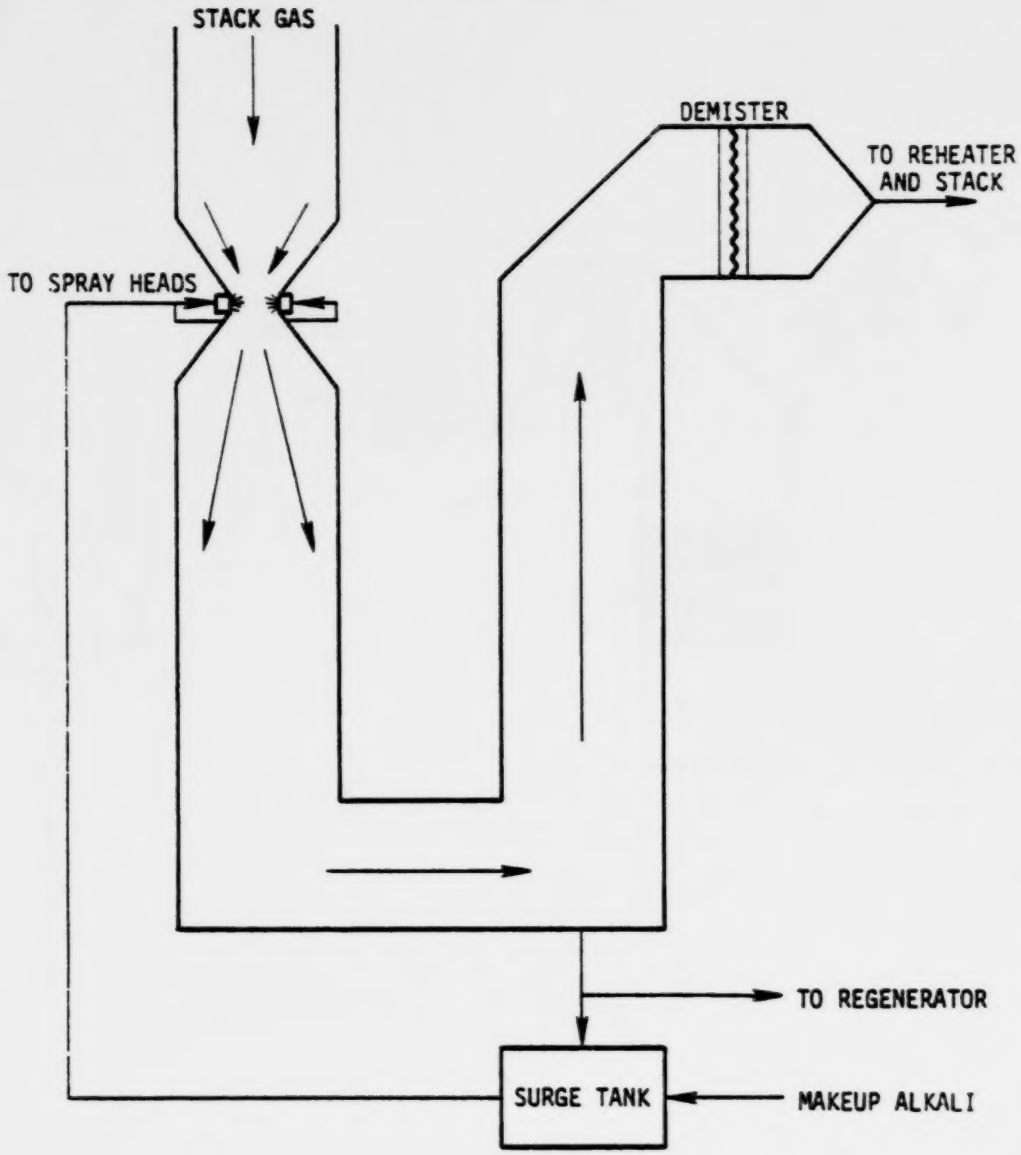


Figure 4. Venturi type absorber.

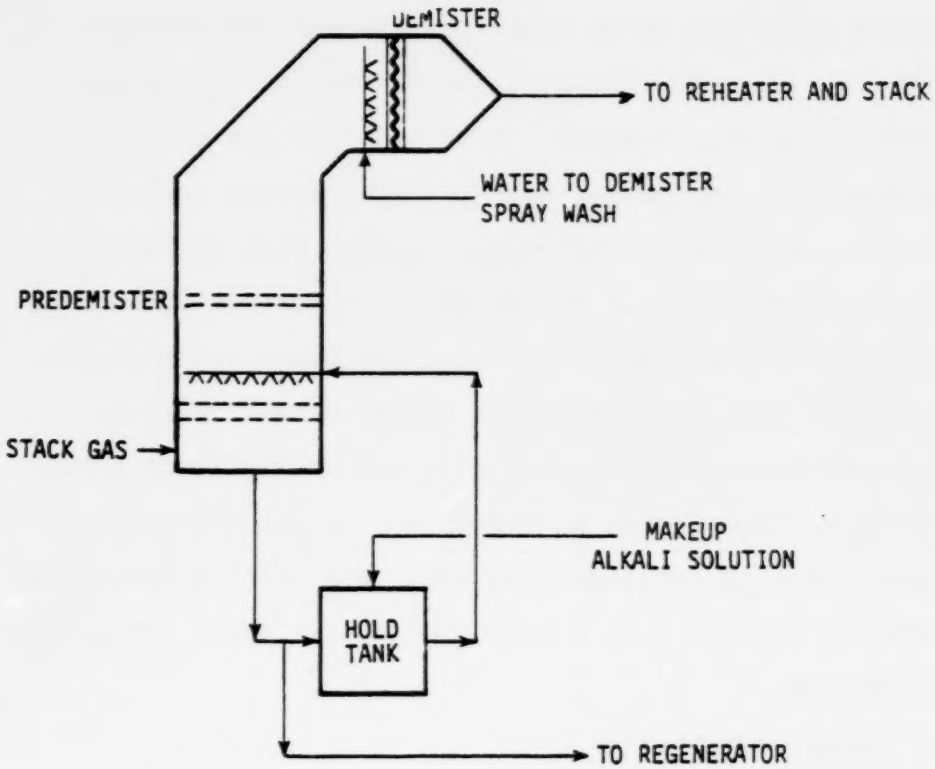


Figure 5. Sieve or perforated tray absorber.

uniform gas-liquid distribution. Absorber module sizes of surveyed systems ranged from 20 to 32 MW, but larger modules are available.

2.2.3 Demister

The demister downstream from the absorber is necessary to remove entrained water droplets, thereby decreasing downstream equipment corrosion and decreasing the energy requirement in the reheater. Mist droplets are generally large enough to be removed with a simple change in gas direction. Mist pad or "Z"-type cyclonic vane demisters are sufficient, and they can be placed in series for additional capacity. Demisters are subject to corrosion and occasionally require the installation of a soot blower or spray wash. Demisters are constructed of either stainless steel or fiberglass reinforced polyester and can be installed in the horizontal or vertical position. The vertical position is shown in Figures 1 to 5 even though horizontal units could be used.

2.2.4 Stack Gas Reheater

It is generally necessary to reheat stack gas to maintain plume dispersion. Reheating also protects downstream equipment (such as ducts and stacks) and prevents acid mist formation. Reheat temperatures generally range from 75° to 95°C. Reheating can be accomplished by installing a gas or

oil burner that exhausts directly into the stack, installing steam coils to heat flue gas, using steam coils to heat air and injecting it into the stack, or by passing some hot flue gas around the scrubber into the stack. Bypassing some hot flue gases tends to increase $SO_2$ emissions. An in-line heat exchanger costs the least initially, but maintenance costs are high because it is subject to corrosion. A number of systems in the United States do not use any reheat.

2.2.5 Regeneration

Regeneration occurs in a continuously stirred tank reactor. The size of the reactor depends on the process, whether a dilute or concentrated mode is used, and whether lime or limestone regeneration is applied. Reaction hold tank time is about 10 times longer for limestone than for lime. Materials of construction for reaction tanks are similar to those of the absorber.

2.2.6 Sludge Disposal

Sludge disposal can require as much as 200,000 $m^2$ for a small plant and 4,000,000 $m^2$ for a large plant. Sludge disposal practices are site specific. A power plant in an arid location might pump the sludge into an unlined pond, allowing the water to evaporate or seep into the ground. In an area where surface runoff or leaching could be a problem, the sludge is sometimes dewatered before being pumped into a

lined pond. The water would be returned to the system or purged after treatment to reduce chloride ions in the slurry. Plants located in areas where land is relatively expensive dewater the sludge to a maximum of 20 percent liquid level by using clarifiers, thickeners, and vacuum filters and then fix the sludge by adding a proprietary compound. Fixation is necessary to make the sludge pond suitable for a construction site at a later date. A totally closed system, where no water is purged into a nearby stream or river, has been achieved in the United States where water pollution regulations require it.* Closed-loop systems are more subject to chloride ion concentration buildup in the slurry, especially when coal is burned.

## 2.3 OPERATING PARAMETERS

### 2.3.1 Chemical Parameters

In a double alkali system, the pH of the absorber is maintained in the range from 6 to 7. A pH of 6.5 is the normal control point. A higher pH increases carbon dioxide adsorption and can lead to carbonate scaling, whereas a lower pH increases the $SO_2$ vapor pressure over the solution and reduces $SO_2$ absorption. Moreover, a solution pH of 6.5 is highly buffered and can adapt rapidly to flue gas inlet

* This was accomplished on a limestone scrubbing system at the Sherburne County Station in Becker, Minnesota.

conditions. A more detailed description of the above phenomenon is presented in Section 4.

The solution from the absorber is pumped to the regeneration reactor. Limestone is added to the calcium sulfite precipitates, and the pH increases to about 7.3.

2.3.2 Physical Parameters

The primary scrubber in the system can be a particulate scrubber or just a gas cooler and humidifier. Flue gas temperature is normally lowered to 55°C to provide adequate $SO_2$ removal. Liquid-to-gas ratios of the surveyed systems range from 0.5 to 1.5 liter/$Nm^3$, flue gas velocities across the throat are about 2 m/s, and pressure drop across the throat is about 3 kPa.

The L/G ratios in the $SO_2$ absorber in these systems vary from 1.5 to 3 liter/$Nm^3$, flue gas velocities in the scrubber from 2 to 7 m/s, and pressure drops across the absorber from 1 to 5 kPa.

Flue gas velocities in a vertical demister average 6 m/s. The optimum flue gas velocity in horizontal demisters is 2.5 m/s. Increasing the velocity increases the water removal rate, but also increases the entrainment of water before it can leave the demister. Pressure drop across the demister ranges from 200 to 500 Pa.

The flue gas is reheated sufficiently (75° to 95°C) to prevent condensation of moisture in the gas. Depending on the method, reheat requires an energy expenditure of approximately 1100 J/kg of flue gas/°C of reheat.

Regeneration tank retention times vary from 10 minutes for lime regeneration to 2 hours for limestone regeneration. The vacuum filter on a 20-MW unit is sized to handle 100 kg/min. The thickener is 9 m in diameter.

## 3.0 CURRENT STATUS, ASSESSMENT, AND PLANS

The double alkali/sludge system is relatively new, even though the basic processes have been used for more than 20 years. Its development resulted from the scaling and plugging problems usually associated with first generation direct lime/limestone systems. The primary scaling and plugging problems are overcome by using a soluble $SO_2$ absorbant and reactant. The system already has proved itself, in pilot plant and industrial-sized boilers, to be a low-maintenance, high-availability system with high lime/limestone utilization operating near the stoichiometric ratio with either high- or low-sulfur coal. The disposal product has good compaction and dewatering properties. The major drawbacks are additional equipment costs for the reaction tank, for water softening, and sludge washing, and costs of sodium to make up for that lost in the sludge and from leaks and spills.

The major areas of concern regarding the applicability of this process are the necessity for a large disposal site and the large quantities of lime or limestone that are required. Most double alkali/sludge process experience, however, has been with lime as opposed to limestone as the

soluble alkali regeneration agent. Lime is substantially more expensive and requires significant quantities of energy for its production from limestone. If the appropriate features discussed in the five modes of operation in Section 2.1.4 are incorporated, the system is very adaptable to the size of boiler, the amount of sulfur in the fuel, and lime and/or limestone available. Additional flexibility can be obtained by using a different absorbant alkali.

Several units are planned for installation in small power plant boilers and industrial-sized boilers. Most users now choosing this system are doing so because of its low maintenance needs and high availability.

Cost studies indicate that double alkali sludge systems are comparable in cost to lime or limestone scrubbing processes. It remains to be seen whether their potential reliability and their advantages in $SO_2$ removal efficiency will be sufficient to displace the more developed lime/limestone processes over the next 5 to 10 years. Double alkali systems seem particularly promising for small industrial boilers where low maintenances and high availability are particularly important.

Table 1 summarizes the status of surveyed double alkali/sludge systems. The ranges of collection efficiencies and availability refer only to the surveyed systems. The rest

Table 1. SUMMARY OF STATUS OF SURVEYED DOUBLE ALKALI/SLUDGE FGD SYSTEMS

| | |
|---|---|
| **All Systems** | |
| Total number of systems in operation by December 1977 | 5 |
| Total number of systems built | 7 |
| Total number of systems surveyed | 2 |
| Year first placed in commercial service | 1974 |
| Number of utility systems using process[a] | 0 |
| Total MW of these facilities | 0 |
| Number of industrial combustion systems | 3 |
| **Surveyed Systems** | |
| Range of average $SO_2$ removal efficiencies, % | 90-99 |
| Range of fly ash removal efficiency by FGD systems, % | 83-99.7 |
| Range of average availability factors[b] | N.A. |

[a] Three utilities will have systems operational in 1979 (representing 1102 MW).

[b] Availability factor computation, see Appendix B.

N.A. - Not available.

of the information refers to all double alkali/sludge systems projected through December 1977. Table 2 presents important characteristics of each surveyed facility, and Appendix A contains questionnaires in which more detailed information can be found.

Table 2. STATUS OF SURVEYED FGD INSTALLATIONS DOUBLE ALKALI/SLUDGE

| Name of plant | Location | Size, MW | Fuel type | Characteristics heat value, S,% | Characteristics heat value, $10^7$ J/kg | Flue gas treated $Nm^3/s$ | Flue gas treated % of total | Year FGD systems started | $SO_2$ removal efficiency, % | Disposition of end products | Energy required,% | Avg. availability,% |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| General Motors Parma | Parma, Ohio | 32 | Coal | 1.6 to 2.9 | 2.91 | 12.8 | 100 | 1976 | 90 | Approved landfill | 3-5[a] | 80 |
| Scholz Gulf Power | Chattahoochee, Florida | 20 | Coal | 0.9 to 5.0 | 2.67 to 3.27 | 26 | 50 | 2/75 to 7/76 | 95 to 99 | Ponded | 2.5[b] | N.A. |

[a] Reheat not used.

[b] In addition 1.7% reheat.

N.A. - not available.

# 4.0 RECENT TECHNOLOGICAL DEVELOPMENTS AND SOLUTIONS TO PROBLEM AREAS

Because of the high solubility of sodium alkalis and their sulfur-containing reaction products, sodium-based double alkali systems are not subject to the scaling and erosion problems generally associated with direct lime/limestone-based systems.

## 4.1 CONTROL OF pH

Maximization of $SO_2$ removal and minimization of scale formation are best achieved by precise control of the scrubber solution pH. A control point of pH 6.5 has been found to be the best for concentrated alkali system reliability and performance. Increasing the pH to above 7 increases carbon dioxide absorption and can lead to calcium carbonate precipitation and possibly to carbonate scaling. Decreasing the pH to below 6 dramatically increases the equilibrium vapor pressure of $SO_2$ in the gas above a concentrated active alkali solution. This can lead to equilibrium-limited scrubbing conditions where outlet concentrations at or below 200 ppm are desired. Graphical evidence

of the phenomenon is provided in Figure 6, in which sulfur dioxide vapor pressure is plotted as a function of pH at a solution temperature of 54°C in a concentrated mode system. In a dilute alkali system the $SO_2$ vapor pressure is much lower.

Operation within the pH range of 6 to 7 is acceptable, but a set point of pH 6.5 is preferred because the sulfite-bisulfite system is highly buffered at that pH, and a highly buffered system is able to adapt to rapidly changing boiler flue gases. In contrast, scrubbing systems operating at a pH of less than 6 can be very sensitive to and adversely affected by rapid changes in flue gas inlet concentrations.

## 4.2 FORMATION OF SULFATES

Sulfate formation in the scrubbing system can seriously affect system performance. Sulfates do not absorb $SO_2$ and are not readily regenerated into an active sodium form by reaction with lime. Sulfate can also form gypsum scale in the presence of calcium ions, thus every attempt is made to suppress oxidation of sulfite to sulfate anywhere in the scrubber system. Oxidation is known to be a function of the rate of oxygen dissolution, scrubbing solution pH, trace contaminants (catalytic effects of fly ash or lime and soda ash impurities), ionic strength of the solution, absorber design, $SO_2$ and $O_2$ concentrations in the flue gas, and flue

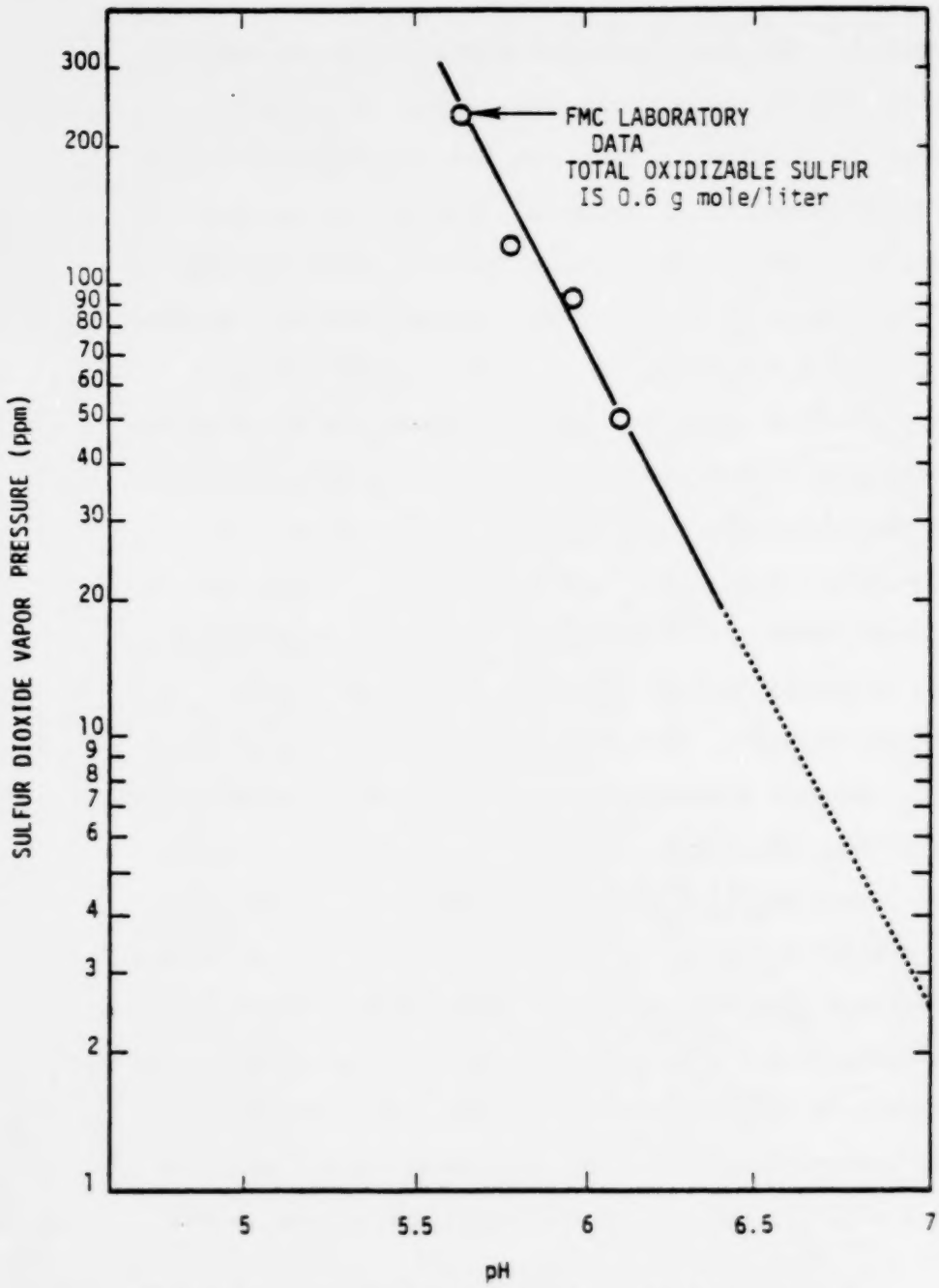


Figure 6. Concentrated active alkali system: sulfur dioxide vapor pressure vs. pH @ 54°C.

(From: the FMC Concentrated Double-Alkali Process, by Legatski L.K., K.E. Johnson, and L.Y. Lee, FMC Corp. Glen Ellyn, Illinois)

gas temperature. Further, because oxidation is strongly influenced by oxygen absorption, the number of contact stages should be limited to two, and the regeneration reactor must be optimized to minimize oxidation. In concentrated systems, unsaturated calcium sulfate operation is maintained by coprecipitation of calcium sulfite and sulfate from slurry liquid saturated in calcium sulfite and unsaturated in calcium sulfate. This produces low sulfite-to-sulfate oxidation rates. Calcium sulfate can be coprecipitated with the principal sulfite precipitate up to a sulfate/sulfite mole ratio of approximately 0.2. Thus, unsaturated conditions can be maintained only at relatively low sulfite oxidation rates, achievable in high $SO_2/O_2$ ratio emission sources. The minimum inlet gas conditions necessary to operate a concentrated-mode system reliably and economically are, therefore, 400 to 500 ppm $SO_2$ and 5 percent $O_2$. A lower $SO_2/O_2$ ratio is unacceptable to the concentrated mode of operation because of the domination of the sulfate species. For flue gas applications that equal or fall below these inlet gas requirements (such as predominate in some industrial boilers, bark boilers, and paper mills), dilute-mode double alkali systems are technically feasible because they can withstand high oxidation rates (up to 100 percent).

## 4.3 CHLORIDE IONS ($Cl^-$)

High chloride concentration in the scrubber system can cause problems. Water, limestone, and especially fuel can bring chloride ion into the system. Coal-burning systems are especially susceptible to buildup of chloride ion concentrations. Chloride ion in the coal at or above 0.04 percent by weight can increase scale development in the scrubber loop. Chloride ion also tends to increase corrosion of internal scrubber parts, reduce the concentration of active sodium, and increase the loss of sodium to the waste stream as sodium chloride (NaCl), causing a potential water pollution problem. The best solution to this problem is to burn low-chloride coal. If this is not possible, a prescrubber with a separate liquor loop should be installed to remove most of the chloride from the flue gas, and the system must be designed against chloride corrosion. Finally, a portion of the recycle liquor stream could be treated to remove chloride. Stringent water pollution control regulations could require the installation of deionizers on the wastewater purge stream. This could add substantially to the cost and require additional sodium makeup.

## 5.0 COST

Available cost data are presented in Table 3. The costs have been escalated to reflect a January 1976 initiation of plant construction, using the Chemical Engineering plant cost index (1957-59 = 100, Jan. 1976 = 187.1). The plant cost index compares the 1976 cost of plant construction with the cost during the 1957-59 period and can be used to determine the cost of any point in between.

General Motors provided itemized annual cost figures, but did not itemize capital costs for its Parma prototype. Gulf Power indicated that the costs associated with the Scholz system would not be applicable because that prototype plant was developed for lime, limestone, and double alkali modes.

Because available cost data were very limited, missing annual costs were estimated.* Reported costs, such as those for electricity and limestone, were used where available in the estimating procedure, otherwise the following were assumed:

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* Ponder, T.C., L.V. Yerino, V. Katari, Y. Shah, and T.W. Devitt. Simplified Procedures for Estimating Flue Gas Desulfurization System Costs. Industrial Environmental Research Laboratory, Research Triangle Park, North Carolina. EPA-600/2-76-150 U.S. Environmental Protection Agency, Washington, D.C., June 1976.

Table 3. COST DATA OF INDIVIDUAL INSTALLATIONS FOR THE DOUBLE ALKALI SLUDGE FGD SYSTEM

| | | | |
|---|---|---|---|
| | Company name | General Motors | Gulf Power |
| | Plant name | Parma | Scholz |
| | Location | Parma, Oh., USA | Chattahoochee, Fl., USA |
| 1. | Reported capital costs, $ | 3,200,000 | |
| | Year | 1974 | N.A. |
| | Cost inflated to 1976 | 4,352,000 | (Pilot plant) |
| | $/kW | 136 | |
| 2. | Reported annual costs, $ | | |
| | Total variable costs | 205,000 | |
| | Total fixed costs | 350,000 | |
| | Fixed charge factor, % | 8.04 | |
| 3. | Boiler operating hours | 4516 | |
| | Capacity factor | 0.51 | |
| | Generated MWh | 142,963[a] | |
| 4. | Reported cost per kWh, mills/kWh | 3.88[b] | |
| | Total cost, mills/kWh[c] 4000h | 3.71 | |
| | 8000h | 4.99 | |
| | Fixed cost boiler operation | 2.49 | |
| | Variable costs | 1.43 | |

[a] Equivalent, this is not an electric utility boiler.

[b] Estimated.

[c] Based on load of 100% for the hours shown.

N.A. - not available.

| | |
|---|---|
| Electricity | 25 mills/kWh |
| Limestone | $16.5/Mg |
| Labor | $10/h |

The life of an FGD was assumed to be 20 years; interim replacement, taxes, insurance, and capital charges came to 0.1365 of the total 1976 capital cost.

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# APPENDIX A

# APPENDIX A

## QUESTIONNAIRE DATA ON THE DOUBLE ALKALI/SLUDGE FLUE GAS DESULFURIZATION PROCESS

| | | [illegible] ENGINEERING Chevrolet Parma | CEA/AIN* Scholz Steam Plant |
|---|---|---|---|
| 1. | GENERAL DESCRIPTION | | |
| 1.1 | Company | General Motors | Gulf Power Co. |
| 1.2 | Plant name | Chevrolet Parma | Scholz Steam Plant |
| 1.3 | Preparer's name and mailing address | Michael D. Giordano<br>11499 Chester Road<br>Cincinnati, Ohio 45246 | T. W. Day<br>11499 Chester Road<br>Cincinnati, Ohio 45246 |
| 1.4 | Principal plant products | Electrical power | Electrical power |
| | Brief description of area surrounding plant site and factors for choice for FGD system | N.A. | N.A. |
| 1.5 | Plant location | Parma, Ohio | Between Chattahoochee and Sneads, Florida |
| 1.6 | STATION CAPACITY | | |
| 1.6.1 | Total boiler generating capacity, MW/number of boilers | 32 | 40/2 |
| 1.6.2 | Capacity served by FGD system, MW | 91.76 | 20 |
| | Amount of flue gas treated, $Nm^3/h$ | | |
| | % of boiler flue gas treated by FGD system | 100 | 50 |
| | Number of boilers served | 6 | 1 |

N.A. - Not available.

$Nm^3/h$ = $m^3/h$ (0°C and 101.325 kPa)

*CEA-Combustion Equipment Associates, Inc.
ADL-Arthur D. Little, Inc.

(continued)

## APPENDIX A (continued)

| | | KOCH-ENGINEERING: Chevrolet Parma | CEA/ADL Scholz Steam Plant |
|---|---|---|---|
| 1.7 | TYPE OF FGD SYSTEM | Double-Alkali-Sludge | Double-Alkali-Sludge |
| 1.8 | Number of scrubber trains in parallel | 4 | 1 |
| 1.9 | FGD system installed on new or existing boiler | Existing | Existing |
| 1.10 | STATUS OF FGD SYSTEM<br>Operational or under construction, date started | Operational, March 1974 | Started, February 1975<br>Shutdown, July 1976 |
| 2. | BOILER DATA | | |
| 2.1 | Boiler identification number | Chevrolet Parma No. 2[a] | No. 14 |
| 2.2 | Maximum continuous heat input, MW | 37.49 | 139.2 |
| 2.3 | Max. cont. net generating capacity, MW | 12 estimated | 47.5 |
| 2.4 | Flue gas flow rate, $Nm^3/h$ temperature at induced draft fan, °C | 74,935<br>200 | 127,440<br>135 |
| 2.5 | Boiler manufacturer | Erie City | Babcock and Wilcox |
| 2.5.1 | Fuel type | Coal | Coal |
| 2.5.2 | Firing configuration | Spreader stoker | Pulverized-coal fired |
| 2.6 | Year placed in service | 1967 | 1953 |
| 2.7 | Type service | Heating load (2 of 4 used usually) | N.A. |
| 2.8 | Stack height, m | 19.8 | 45.7 |
| 2.8.1 | Flue gas exit velocity, m/s | N.A. | 13.9 |
| 2.9 | Average boiler operation, h/yr | 4516/1976 | N.A. |
| 2.10 | Average boiler capacity factor | 0.51 | N.A. |

[a] Section 2 is for boiler No. 2 only.



(continued)

APPENDIX A (continued)

| | | KOCH-ENGINEERING Chevrolet Parma | CEA/ADL Scholz Steam Plant |
|---|---|---|---|
| 2.11 | COAL COMPOSITION | | |
| 2.11.1 | Lower heating value, kJ/kg | 29,168 | 26,800-32,800 |
| 2.12.2 | Sulfur content, % | 1.66-2.89 | 0.9-5.0 |
| 2.11.3 | Ash content, % | 4.99-10.7 | 14.0 |
| 2.11.4 | Chloride content, % | N.A. | 0.02-0.15 |
| 2.11.5 | Moisture, % | 5.0 | 15.0 |
| 2.12 | OIL COMPOSITION | N.A. | N.A. |
| 2.12.1 | Grade/heating value, kJ/kg | | |
| 2.12.2 | Sulfur content, % | | |
| 2.12.3 | Ash content, % | | |
| 2.12.4 | Chloride content, % | | |
| 2.13 | PARTICULATE REMOVAL EQUIPMENT NOT PART OF FGD SYSTEM | | |
| 2.13.1 | Type | Mechanical | Electrostatic Precipitators |
| 2.13.2 | Manufacturer | Western Prec. | Buell |
| 2.13.3 | Efficiency, % removal | 92 (design) | 99.7 (design) |
| 2.13.4 | Emission rate | 0.43 kg/GJ | Below 45.8 $mg/m^3$ |

(continued)

## APPENDIX A (continued)

| | | KOCH-ENGINEERING<br>Chevrolet Parma | CEA/ADL<br>Scholz Steam Plant |
|---|---|---|---|
| 3. | EMISSION REGULATIONS | | |
| 3.1 | ATMOSPHERE EMISSIONS | | |
| 3.1.1 | $SO_2$, ng/kJ | 0.0129 | 0.516 |
| 3.1.2 | Particulate, ng/kJ | 0.0086 | 0.043 |
| 3.1.3 | $NO_x$, ng/kJ | N.A. | 0.301 |
| 3.1.4 | Other | N.A. | None |
| 3.1.5 | Legal basis | N.A. | Florida state code |
| 3.2 | RESTRICTIONS APPLICABLE TO LIQUID OR SOLID WASTES/LEGAL BASIS | No liquid is discharged from system. Solid waste is disposed of at a local land fill approved by the Ohio EPA. | N.A. |
| 4. | FGD SYSTEM INFORMATION | | |
| 4.1 | Process name | Double alkali scrubbing | Dual alkali |
| 4.1.1 | Supplier or design company | Koch-Engineering | CEA/ADL |
| 4.1.2 | WHY WAS THIS SYSTEM CHOSEN? | Reliability over limestone system | N.A. |
| 4.1.3 | PROCESS DESCRIPTION | $SO_2$ absorbed by regenerated caustic solution forming soluble sodium salt soln. regenerates caustic, and reduces scaling. | $SO_2$ absorbed by sodium sulfite soln., regenerated with lime/ limestone soln. and solids separated for waste. |

(continued)

## APPENDIX A (continued)

| | | KOCH ENGINEERING Chevrolet Parma | CEA/ADL Scholz Steam Plant |
|---|---|---|---|
| 4.2 | $SO_2$ SCRUBBING AGENT | | |
| 4.2.1 | Name | Caustic plus soda ash makeup (0.1 N NaOH) | Sodium solution |
| 4.2.2 | Chemical composition | $Na_2CO_3$ - NaOH | $Na_2SO_3$ - NaOH - $Na_2CO_3$ |
| | Components, % by weight | N.A. | $Na_2SO_3$, varied<br>NaOH, varied<br>$Na_2CO_3$, varied |
| 4.2.3 | Stoichiometric requirement | 100% 0.1N concentration | 0.03 |
| 4.2.4 | Addition rate, kg/h | N.A. | Varied |
| 4.2.5 | Particle size, mm | N.A. | N/A |
| 4.3 | REGENERATION AGENT | | |
| 4.3.1 | Name | Lime (slurry) | Lime and/or limestone |
| 4.3.2 | Composition, % | $CaO + H_2O$ | $Ca(OH)_2$, 88-95 $CaCO_3$, 88-95 |
| 4.3.3 | Stoichiometric requirement | 1.1 - 1.5/mole S in fuel | 0.95 - 1.0/mole S in fuel |
| 4.3.4 | Addition rate | N.A. | Varied |
| 4.3.5 | Particle size | N.A. | N/A |
| 4.4 | SALABLE PRODUCT | None | None |
| 4.4.1 | Name | | |
| 4.4.2 | Chemical composition<br>Components, % by weight ton | | |
| 4.4.3 | Amount generated/year, ton/yr | | |
| 4.4.4 | Sales potential | | |



(continued)

## APPENDIX A (continued)

| | | KOCH-ENGINEERING Chevrolet Parma | CEA/ADL Scholtz Steam Plant |
|---|---|---|---|
| 4.4.5 | BY-PRODUCT RECOVERY PROCESS<br>Name<br>Vendor<br>Process description | None | None |
| 4.4a | Intermediate product composition | | |
| 4.5 | BY-PRODUCT NO. 2 | None | None |
| 4.6 | WASTE STREAMS | | |
| 4.6.1 | Type of waste | Sludge Stream | Filter cake |
| | % water | 40-50 | 30-45 |
| 4.6.2 | Amount generated in one hour at full load, kg/h | 2903 | 1168-5436 |
| 4.6.3 | Disposal method | Landfill | Trucked |
| 4.6.4 | Disposal site and distance from plant, km | 4.8-6.4 | On-site pond |
| 4.6.5 | Potential effects on environment from sludge disposal | None | N.A. |
| 4.7 | SLUDGE FIXATION PROCESS | None | None |



(continued)

## APPENDIX A (continued)

| | | KOCH-ENGINEERING Chevrolet Parma | CEA/ADL Scholz Steam Plant |
|---|---|---|---|
| 4.8 | FGD EQUIPMENT DATA | | |
| 4.8.1 | FIRST SCRUBBER | | |
| 4.8.1.1 | Type | Multi-venturi flexitray impingement | Venturi |
| 4.8.1.2 | L/G[a] $\ell/Nm^3$ | 25.2 | 40-80 (saturated) |
| 4.8.1.3 | Gas velocity through absorber or scrubber, m/s | 1.524-4.57 | 2.7-3.0 |
| 4.8.1.4 | Absorbent (adsorbent) flow, $m^3/h$ | N.A. | 68.4-136.8 |
| 4.8.1.5 | Gas flow entering scrubber, $Nm^3/h$ | 103,600 (Nu. 2 boiler) | 127,440 |
| 4.8.1.6 | Gas temperature, °C | 199 | 135 |
| 4.8.1.7 | Gas composition | | |
| | $SO_2$ in + out, ppm | 800-1300 + 80-130 | Varies (not measured) |
| | % removal | 90 | N.A. |
| | Particulate in + out | 430 g/GJ + 81.7 g/GJ | N.A. + Below 45.8 $mg/m^3$ |
| | % removal | 81 | N.A. |
| | $NO_x$ in + out, ppm | N/A | N.A. |
| | $CO_2$ in + out, ppm | 6-12% + 6-12% | N.A. |
| | Other in + out | N.A. | N.A. |
| 4.8.1.8 | Material of construction | 316L SS welded | Carbon steel |
| 4.8.1.9 | Type of lining | 316L SS non-welded | Flakeline |
| 4.8.1.10 | Adsorbent and sand losses | N.A. | N.A. |
| 4.8.1.11 | Number of stages | 1 | 1 |
| 4.8.1.12 | Packing type and composition | N.A. | None |

[a] Liquid-to-gas ratio



(continued)

## APPENDIX A (continued)

| | | KOCH-ENGINEERING Chevrolet Parma | CEA/ADL Scholz Steam Plant |
|---|---|---|---|
| 4.8.2 | SECOND SCRUBBER | None | |
| 4.8.2.1 | Type | | Tower |
| 4.8.2.2 | L/G ratio, $\ell/Nm^3$ | | 40-80 (saturated) |
| 4.8.2.3 | Gas velocity through absorber or scrubber, m/s | | 2.7-3.0 |
| 4.8.2.4 | Absorbent (adsorbent) flow, $m^3/h$ | | 68.4-136.8 |
| 4.8.2.5 | Gas flow entering scrubber, $Nm^3/h$ | | 101,880 |
| 4.8.2.6 | Gas temperature, °C | | 49-60 |
| 4.8.2.7 | Gas composition | | |
| | $SO_2$ in + out, ppm | | 900-1400 + Below 100 |
| | % removal | | 95-99 (actual) |
| | Particulate in + out, $mg/Nm^3$ | | Below 45.8 + Below 45.8 |
| | % removal | | N.A. |
| | $NO_x$ in + out, ppm | | N.A. |
| | % removal | | N.A. |
| | $CO_2$ | | N.A. |
| | Other | | N.A. |
| 4.8.2.8 | Material of construction | | Carbon steel |
| 4.8.2.9 | Type of lining | | Flake lined |
| 4.8.2.10 | Number of stages | | 1 |
| 4.8.2.11 | Packing type and composition | | None |

(continued)

## APPENDIX A (continued)

| | | BOCH-ENGINEERING Chevrolet Parma | CEA/ADL Scholz Steam Plant |
|---|---|---|---|
| 4.8.3 | CLEAR WATER TRAY | | |
| 4.8.3.1 | Type | None | Sieve tray |
| 4.8.3.2 | L/G ratio, $\ell/Nm^3$ | | 40-80 (saturated) |
| 4.8.3.3 | Source of water | | Recirculated and regenerated |
| 4.8.4 | DEMISTER | | |
| 4.8.4.1 | Type | Flexmesh | Chevron |
| 4.8.4.2 | Number of passes (stages) | 1 | 4 |
| 4.8.4.3 | Material of construction | Plastic polypropylene | Polypropylene |
| 4.8.4.4 | Method of cleaning | Manual | Wash tray |
| 4.8.4.5 | Flow rate during cleanings, $Nm^3/h$ | N.A. | 0 |
| 4.8.4.6 | Frequency and duration of routine cleaning | Once each 6 month period. | No cleaning required. |
| 4.8.5 | REHEATER | | |
| 4.8.5.1 | Type | Not in use | Direct fired |
| 4.8.5.2 | Heat load, kW | | 1060 |
| 4.8.5.3 | Heat transfer surface area, $m^2$ | | N.A. |
| 4.8.5.4 | Temperature of gas in, °C<br>out, °C | | 52<br>79 |
| 4.8.5.5 | Reheater materials of construction | | Carbon steel |

(continued)

## APPENDIX A (continued)

| | | KOCH ENGINEERING Chevrolet Parma | CEA/ADL Scholz Steam Plant |
|---|---|---|---|
| 4.8.6 | SCRUBBER TRAIN PRESSURE DROP, mbar | | |
| 4.8.6.1 | First scrubber | 19.0-24.9 | N.A. |
| 4.8.6.2 | Second scrubber | N.A. | N.A. |
| 4.8.6.3 | Clear water tray | N.A. | N.A. |
| 4.8.6.4 | Demister | 0.498 | N.A. |
| 4.8.6.5 | Reheater | N.A. | N.A. |
| 4.8.6.6 | Ductwork | N.A. | N.A. |
| 4.8.6.7 | Total FGD system | N.A. | 49.8 |
| 4.8.6.8 | I.D fan | N.A. | 54.8 |
| 4.9 | SYSTEM MAKEUP WATER ADDED, $m^3/h$ | 2.268-1.368 | N.A. |
| 4.9.1 | Water added per mole of $SO_2$ removed, $m^3/kg$ mol | N.A. | |
| 4.9.2 | Source of makeup water | City water | |
| 4.9.3 | Where is water added | Pump seals, cake washing and lime slaking | |
| 4.10 | BYPASS SYSTEM | | N.A. |
| 4.10.1 | Can flue gas be bypassed? | Yes | |
| 4.10.2 | Height of gas discharge when bypassed, m | 19.8 | |
| 4.11 | SLURRY DATA, pH, % SOLIDS BY WEIGHT | N.A. | |
| 4.11.1 | Fresh slurry to scrubber | | 10-12.6/N.A. |
| 4.11.2 | Recirculating slurry | | 6.8-7.0/N.A. |
| 4.11.3 | Waste slurry | | N.A./30 |

(continued)

APPENDIX A (continued)

| | | KOCH-ENGINEERING Chevrolet Parma | CEA/ADL Scholz Steam Plant |
|---|---|---|---|
| 4.12 | SPENT SLURRY SYSTEM | | |
| 4.12.1 | Clarifiers | | |
| 4.12.1.1 | Number | 2 | 1 |
| 4.12.1.2 | Diameter, m | 18.3 | 12.2 |
| 4.12.2 | Solid separation | | |
| 4.12.2.1 | Type | Ametek | Vacuum filter |
| 4.12.2.2 | Cloth area, $m^2$ | 46.5 | 6.97 |
| 4.12.2.3 | Capacity (wet cake), ton/h | 1.80 sludge/h | 5.43 |
| 4.13 | SPACE REQUIRED, EXCLUSIVE OF SLUDGE DISPOSAL AREA, $m^2$ | N.A. | N.A. |
| 4.14 | PERSONNEL, man-hours/yr | | N.A. |
| 4.14.1 | Operating | N.A. | |
| 4.14.1.1 | Specialists | 4 persons | |
| 4.14.1.2 | Unskilled | 2 persons | |
| 4.14.2 | Maintenance and repair | 2 persons | |
| 4.15 | ENVIRONMENTAL LOAD | | |
| 4.15.1 | Wastewater treatment process | N.A. | N.A. |
| 4.15.2 | Concentrations | N.A. | N.A. |
| 4.15.3 | Appearance of flue gas discharge -any mist problems? | Yes | Opacity - 0-10% No mist problems. |

(continued)

## APPENDIX A (continued)

| | | RICH-ENGINEERING Chevrolet Parma | CEA/ADL Scholz Steam Plant |
|---|---|---|---|
| 4.16 | FGD SYSTEM OPERATION | | |
| 4.16.1 | % of boiler load FGD can operate | 80 | 25-100 |
| 4.16.2 | Lag time | None | None |
| 5. | ACTUAL COSTS FOR TOTAL FGD INSTALLATION, year | 1976 | Not applicable. |
| 5.1 | CAPITAL COSTS, $ | See Table C | This was a prototype developed for lime, limestone, particulate and dual alkali modes. |
| 5.1.1 | Scrubber | N.A. | N.A. |
| 5.1.2 | Absorbent/regeneration system | N.A. | N.A. |
| 5.1.3 | Sludge disposal system | N.A. | N.A. |
| 5.1.4 | Site improvements | N.A. | N.A. |
| 5.1.5 | Land, roads, tracks, substation | N.A. | N.A. |
| 5.1.6 | Engineering costs | N.A. | N.A. |
| 5.1.7 | Contractor's fee | N.A. | N.A. |
| 5.1.8 | Interest during construction | N.A. | N.A. |
| | Construction period, mo | 24 | 24 |
| 5.1.9 | License fees | N.A. | N.A. |
| 5.1.10 | Other, $ | N.A. | N.A. |
| 5.1.11 | Total, $ | N.A. | N.A. |



(continued)

APPENDIX A (continued)

| | | KOCH-ENGINEERING Cheverolet Parma | CEA/ADL Scholz Steam Plant |
|---|---|---|---|
| 5.2 | ANNUAL COSTS, $ | N.A. | N.A. |
| 5.2.1 | Interest | | |
| 5.2.2 | Depreciation | | |
| 5.2.3 | Insurance and taxes | | |
| 5.2.4 | Total fixed costs | | |
| 5.2.5 | Labor and overhead<br>Average man-hour cost<br>cost/year | | |
| 5.2.6 | Raw material breakdown<br>Unit cost<br>Annual cost | | |
| 5.2.7 | Utilities, unit cost, annual costs<br>Electricity<br>Water<br>Steam<br>Fuel | | |
| 5.2.8 | Maintenance cost/year | | |
| 5.2.9 | Other costs, list | | |
| 5.2.10 | Total variable cost/year | | |
| 5.2.11 | Total annual cost | | |
| 5.3 | WASTE DISPOSAL COST, $<br>Unit cost<br>Annual cost | N.A. | N.A. |
| 5.4 | BY-PRODUCT CREDIT, $ | N.A. | N.A. |
| 5.4.1 | By-product 1 | | |
| 5.4.2 | By-product 2 | | |

(continued)

APPENDIX A (continued)

| | | KOCH ENGINEERING Chevrolet Farms | CEA/ADL Scholz Steam Plant |
|---|---|---|---|
| 5.5 | NET ANNUAL COST, mills/kWh | N.A. | N.A. |
| 5.5.1 | Cost last year | | |
| 5.5.2 | Cost at maximum continuous rating | | |
| 5.5.3 | Cost without FGD | | |
| 6. | ENERGY REQUIREMENTS, kW | | |
| | Pumps | N.A. | N.A. |
| | Fan | N.A. | N.A. |
| | Reheat | N.A. | N.A. |
| | Reductant chemicals | N.A. | N.A. |
| | Other | N.A. | N.A. |
| | Total | 3-5% of boiler load required for energy to run FGD system. | 500 |

(continued)

APPENDIX A (continued)

| | ROCH-ENGINEERING Cheverolet Perma | CEA/ADL Scholz Steam Plant |
|---|---|---|
| 7. PERFORMANCE HISTORY: OPERATING PROBLEMS AND SOLUTIONS | | |
| 7.1 Scrubber system | $CaCO_3$ and $CaSO_3$ plugging solved with pH control. No current problems. | Appendix Table A |
| 7.2 Demister | Improper design is currently causing inadequate mist elimination. | None |
| 7.3 Reheater | None | Appendix Table A |



(continued)

## APPENDIX A (continued)

| | BOCH-ENGINEERING Chevrolet Parma | CEA/ADL Scholz Steam Plant |
|---|---|---|
| 7.4 Fan | N.A. | Appendix Table A |
| 7.5 Sludge system | Poor clarification due to hindered settling problem caused by high sludge concentration in clarifier reactor. Solved by removing external sludge recycle. | None |
| 7.6 Regeneration system | Gravity flow lines were replaced by open flume to prevent plugging between clarifier No. 2 and mix tanks. | None |
| 7.7 By-product system | None | N/A |
| 7.8 Other | Spray pattern on vacuum filter had to be altered to prevent premature cake cracking. | Appendix Table A |
| 7.9 Availability, %[a] | 80 | Appendix Table B |

[a] For availability calculation method see Appendix B.

Table A. SUMMARY OF THE PROBLEMS AND SOLUTIONS IN OPERATION OF CEA/ADL PROTOTYPE SCRUBBER

| Unit operation area | Problem | Solution |
|---|---|---|
| Scrubber-absorber module | Failure of rubber linings in bleed control valves. | Replaced with stainless steel valves. |
| Regeneration reactor | Plugging of dry lime feed chute to first stage of | Installation of feed vibrator. |
| | Solids deposition in first stage of multistage | Design and installation of a new first-stage unit. |
| | Broken agitator blade in second stage of multistage reactor. | Part replacement. |
| | Erosion and plugging of Flow-through pH meters | Replaced with immersion type meter with sonic cleaners. |
| Thickener | Plugging of thickener underflow lines. | Installation of flexible lines and addition of back-flushing procedures. |
| | Deterioration of thickner | Patch/replace lining section. |
| Vacuum filter | Erosion and cracking of fiberglass scraper and rocker arm. | Replaced with stainless steel parts. |
| | Erosion of plastic bridge valve. | Part replacement. |
| | Holes in filter cloth. | Repaired holes. |
| | Loss of vacuum due to cracks in trunnion tubes. | Patched cracks. |
| | Insufficient agitation. | New agitation system. |
| Sodium carbonate addition | Plugging in dry feeder gate | Replaced feed control unit. |
| | Insufficient reliability of sodium make-up feed solution. | Revised monitoring system and employed manual techniques. |

Table A (continued).

| Unit operation area | Problem | Solution |
|---|---|---|
| Reheater | Deterioration of refractory in burner chamber. | Replaced refractory material. |
| Fans | Fly ash buildup on fan blade. | Clean and rebalance fan. |
| | Deterioration of thrust bearing. | Part replacement. |
| Pumps | Leakage of scrubber recycle pumps through pump seals and seals and piping. | Replaced packing and flange gaskets. |
| | Broken shaft on reactor pump. | Part replacement. |
| | Failure of reactor pump isolation valves. | Overhauled. |
| | Freezing of pump seal water rotameters. | Replaced parts and modified operating procedures. |
| Tanks | Cracks and pinholes in the lining of the absorber recycle tank. | Repaired. |
| | Plugging of pH meter on recycle tanks. | Repaired and relocated sampling lines. |
| | Liner failure in the thickener hold tank. | Replaced. |
| | Insufficient reliability of level transmitter in the thickener hold tank. | Replaced. |
| Piping | Circuitry failure in heat tracing. | Replaced. |
| Stack | Failure of stack lining. | Repair/replace. |

Table B. CEA/ADL DUAL ALKALI PERFORMANCE HISTORY

| Period | Total period, hr | Boiler operation, hr | FGD operation, hr | FGD[a] operability, percent | FGD[b] utilization, percent |
|---|---|---|---|---|---|
| Feb. 75 | 672 | 459 | 454 | 98.9 | 67.6 |
| Mar. 75 | 744 | 507 | 485 | 95.7 | 65.2 |
| Apr. 75 | 720 | 604 | 336 | 55.6 | 45.2 |
| May 75 | 744 | 598 | 375 | 63.2 | 50.4 |
| Jun. 75 | 720 | 720 | 720 | 100.0 | 100.0 |
| Jul. 75 | 744 | 683 | 221 | 32.4 | 29.7 |
| Aug. 75 | 744 | 744 | 0 | 0 | 0 |
| Sep. 75 | 720 | 577 | 254 | 44.0 | 35.3 |
| Oct. 75 | 744 | 559 | 559 | 100.0 | 75.1 |
| Nov. 75 | 720 | 620 | 560 | 90.3 | 77.8 |
| Dec. 75 | 744 | 732 | 732 | 100.0 | 98.4 |
| Jan. 76 | 744 | 0 | 0 | 0 | 0 |
| Feb. 76 | 696 | 0 | 0 | 0 | 0 |
| Mar. 76 | 744 | 480 | 445 | 92.7 | 59.8 |
| Apr. 76 | 720 | 642 | 616 | 95.9 | 85.6 |
| May 76 | 744 | 735 | 651 | 88.6 | 87.5 |
| Jun. 76 | 720 | 656 | 641 | 97.7 | 89.0 |

[a] FGD operability: The number of hours the FGD system was in operation divided by the number of hours the boiler was in operation, expressed as a percentage.

[b] FGD utilization: The number of hours the FGD system was in operation divided by the number of hours in the period, expressed as a percentage.

Table C. CAPITAL COSTS OF CHEVROLET'S PARMA FACILITY

| Total Capital Cost: | $3,200,000 | (32,841 Mg coal) |
|---|---|---|
| | 1976 costs, $ | $/Mg coal |
| Capital Charge | 350,000 | 7.61 |
| Chemicals | 26,525 | 0.81 |
| Utilities | 33,775 | 1.03 |
| Solid Waste | 46,080 | 1.40 |
| Labor | 113,404 | 3.45 |
| Maintenance | 77,204 | 2.35 |
| | 546,998 | 16.65 |

$16.65/Mg coal total cost of ownership.

# APPENDIX B

## APPENDIX B

### Availability Factor Computation

1. Divide boiler capacity by the number of modules and obtain MW/module = x

2. Multiply boiler capacity by number of hours during selected period (MW) = a

3. Add all down times due to module trouble for all modules during selected period = b

4. Add all down times due to boiler trouble or reduction in electricity demand for all modules during period = c

5. Availability factor = $\frac{[a - x\ (b + c)]\ 100}{a - x\ c}$ = %

# APPENDIX C

## APPENDIX C. CONVERSION FACTORS USED IN THIS STUDY

| Multiply | | By | To Obtain |
|---|---|---|---|
| ft | x | 0.30480 | m |
| $ft^3$ | x | 28.317 | liter |
| Btu/lb | x | 0.55554 | kcal/kg |
| | x | 2.32593 | kJ/kg |
| Btu/h | x | $0.29300 \cdot 10^{-3}$ | kW |
| acfm | x | 1.6992 | $m^3/h$ |
| $lb/10^6$ Btu | x | 1.80005 | mg/kcal |
| | x | 0.42993 | mg/kJ |
| gal/min | x | 3.78541 | liter/min |
| | x | 0.22712 | $m^3/h$ |
| gal/1000 $ft^3$ | x | 0.13368 | liter/$m^3$ |
| $ft^3$/min | x | 1.6992 | $m^3/h$ |
| kcal | x | 4.1868 | kJ |
| kcal | x | $1.163 \cdot 10^{-3}$ | kWh |
| scfm | x | 1.60776 | $Nm^3/h$ |
| gr/$ft^3$ | x | 2.288 | g/$m^3$ |
| gr/scfm | x | 2.4182 | g/$Nm^3$ |
| in. $H_2O$ | x | 0.2488 | kPa |
| in. $H_2O$ | x | 2.54 | mbar |
| gr | x | 0.0648 | g |
| ton (short) | x | 1.9072 | metric ton |

1 MW corresponds to 3200 to 3500 $m^3/h$ flue gas (coal)

1 scfm = 28.317 l (60°F / 14.7 psia)
(15.5°C / 760.28 torr)

26.796 l (0°C/760 torr) = 0.026796 $Nm^3$

1 $SO_2$ = 2.927 g/liter

MW = electric power generated unless other wise specified